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Description

Emulsifier-free finely disperse systems of the water-in-oil type

The present invention relates to emulsifier-free finely disperse systems of the water-in-oil type, preferably as cosmetic or dermatological preparations. In particular, the present invention relates to cosmetic and dermatological preparations having effective protection against harmful oxidation processes in the skin, but also for the protection of cosmetic preparations themselves or for the protection of the constituents of cosmetic preparations against harmful oxidation processes.

Moreover, the invention also relates to cosmetic and dermatological preparations which comprise antioxidants. In a preferred embodiment, the present invention relates to cosmetic and dermatological preparations for the prophylaxis and treatment of cosmetic or dermatological changes in the skin, such as, for example, skin aging, in particular skin aging caused by oxidative processes.

The present invention accordingly relates, in preferred embodiments, to cosmetic or dermatological preparations comprising active ingredients for the care and for the protection of the skin, in particular sensitive skin and, very particularly, skin aging or aged by intrinsic and/or extrinsic factors.

The present invention further relates to cosmetic and dermatological light protection formulations. In addition, the present invention relates to preparations for the cosmetic and dermatological treatment or prophylaxis of erythematous, inflammatory, allergic or autoimmune-reactive phenomena, in particular dermatoses.

The harmful effect of the ultraviolet part of solar radiation on the skin is generally known. The rays have various effects on the skin as an organ depending on their particular wavelength:

UV-C radiation with a wavelength below 290 nm is absorbed by the ozone layer in the earth's atmosphere and therefore has no physiological significance. By contrast, rays in the range between 290 nm and 320 nm, the UV-B region, cause erythema, simple sunburn or even burns of greater or lesser severity. A maximum for the erythema activity of sunlight is given as the relatively narrow range around 308 nm.

Numerous compounds are known for protecting against UV-B radiation; these are mostly derivatives of 3-benzylidenecamphor, of 4-aminobenzoic acid, of cinnamic acid, of salicylic acid, of benzophenone and also of 2-phenylbenzimidazole.

It has for a long time been incorrectly assumed that the long-wave UV-A radiation with a wavelength between 320 nm and 400 nm has only a negligible biological effect and that, accordingly, the UV-B rays are responsible for most of the photodamage to human skin. However, it has in the meantime been demonstrated by numerous studies that UV-A radiation is far more hazardous than UV-B radiation with regard to the triggering of photodynamic, specifically phototoxic, reactions and chronic changes in the skin. The harmful effect of UV-B radiation can also be further intensified by UV-A radiation.

Thus, it has been proven, inter alia, that even UV-A radiation under entirely normal everyday conditions is sufficient to damage, within a short time, the collagen and elastin fibers which are of essential importance for the structure and strength of the skin. This results in chronic light-induced skin changes - the skin "ages" prematurely. The clinical appearance of skin aged by light includes, for example, wrinkles and lines and an irregular, furrowed relief. In addition, the areas affected by light-induced skin aging may have irregular pigmentation. The formation of brown spots, keratoses and even carcinomas or malignant melanomas is also possible. Skin aged prematurely by everyday UV exposure is additionally characterized by a lower activity of the Langerhans cells and a slight chronic inflammation.

In addition, even very low doses of radiation can trigger photochemical reactions. These include, in particular, the formation of free radicals, which may in turn, as a result of their high reactivity, trigger uncontrolled secondary reactions. In order to prevent such reactions, antioxidants and/or free-radical scavengers can be additionally added to the cosmetic or dermatological formulations. Thus, for example, it has been proposed to use vitamin E, a substance with known antioxidative action, in light protection formulations, although the effect achieved here falls a long way short of the desired effect.

Approximately 90% of the ultraviolet radiation which reaches the earth consists of UV-A rays. Whereas UV-B radiation varies greatly depending on numerous factors (e.g. season and time of day or latitude), UV-A radiation remains relatively constant from day to day irrespective of seasonal and diurnal or geographic factors. At the same time, most of the UV-A radiation penetrates into the living epidermis, while approximately 70% of the UV-B rays are retained by the horny layer.

Sunbathing is regarded by most people as pleasurable, and the disadvantageous consequences are initially not taken into account. However, in recent years, knowledge about the negative effects of excessively intensive solar irradiation has emerged, for which reason a greater number and more strongly protecting sunscreens are applied.

Since the contributions of the various wavelength ranges of UV light to light-induced skin changes have not been fully explained, it is nowadays increasingly assumed that preventive protection both against UV-A and also against UV-B rays, for example by applying light protection filter substances in the form of a cosmetic or dermatological formulation to the skin, is of fundamental importance. Cosmetic or dermatological compositions are intended, when applied to the skin in a thin layer, to protect it against the negative effects of solar radiation.

Generally, the light absorption behavior of light protection filter substances is very well known and documented, especially since most industrialized countries have positive lists for the use of such substances, which impose very strict standards on the documentation. Depending on which UV light range absorption takes place, a distinction is made between UV-B filters, UV-A filters and broadband filters (which have a filter effect over the entire UV-A and UV-B region). Through appropriate choice of the UV filter and its concentration in the sunscreen, it is possible to influence the degree of shielding of UV light. For the concentration of the substances in the finished formulations, the absorbance values can at best be a guide, since interactions with ingredients of the formulation or of the skin itself may result in imponderables. In addition, it is usually difficult to estimate beforehand how uniformly and thickly the filter substance is distributed in and on the horny layer of the skin.

The effectiveness of sunscreens or of the UV filters on which they are based is generally determined in biological effectiveness tests under standardized conditions.

The light protection factor (LPF, also often called SPF (**Sun Protection Factor**)) gives the extension of solar irradiation permitted as a result of use of the sunscreen. It is the quotient of the erythema threshold time with sunscreen and erythema threshold time without sunscreen.

To test the UV-A protection performance, use is usually made of the IPD method (IPD \equiv Immediate **Pigment Darkening**). Similarly to the determination of the light protection factor, this method gives a value which indicates how much longer the skin protected with the light protection composition can be irradiated with UV-A radiation until the pigmentation which occurs is the same as for the unprotected skin.

Another test method which has become established throughout Europe is the Australian Standard AS/NZS 2604:1997. In this test, the absorption of the preparation in the UV-A region is measured. In order to satisfy the standard, the preparation must absorb at least 90% of the UV-A radiation in the region 320 -360 nm.

Most sunscreens are applied in the vicinity of water or during sporting activity (perspiration), for which reason the water resistance of such formulations is to be attributed particular importance. A water-resistant sunscreen protects the user not only after bathing, but also protects him against sunburn during bathing.

In order to achieve high light protection factors coupled with very good water resistance, W/O formulations are advantageous. However, W/O emulsions of the prior art frequently have unsatisfactory cosmetic properties. During application, corresponding preparations can leave behind a greasy, shiny and sometimes sticky impression on the skin and - particularly on hairy skin - are difficult to spread. In individual cases, therefore, such preparations may not even be marketable since they are unacceptable to or viewed negatively by the consumer.

An object of the present invention was therefore to remedy the disadvantages of the prior art and to find preparations of the water-in-oil type which, for example, permit the formulation of high light protection factors coupled with very good water resistance, but which do not leave behind a greasy or sticky impression.

Light dermatoses are generally triggered by UV-A radiation. The most frequent of all photodermatoses is polymorphous light dermatosis (PLD), which is, inter alia, also referred

to as sun allergy or Mallorca acne and a large number of other names, as given in the literature (e.g. A. Voelckel et al, *Zentralblatt Haut- und Geschlechtskrankheiten* (1989), 156, p.2).

Over 20% of the white population in industrialized countries in the northern hemisphere are affected by PLD. After the first relatively intensive solar irradiation in spring, patients usually firstly suffer from irritation and the formation of areal skin reddening in the region of sun-exposed areas of skin (face, neck, décolletage and arms and legs), and as time passes small nodules, plaques, vesicles or papules may also arise.

Erythematous skin symptoms also occur as accompanying symptoms in certain skin disorders or irregularities. For example, the typical skin rash symptom of acne is generally red to a greater or lesser extent.

Accordingly, it was also an object of the invention to provide cosmetic, dermatological and pharmaceutical preparations and light protection formulations which serve for the prophylaxis and treatment of light-sensitive skin, in particular photodermatoses, preferably PLD.

Antioxidants are mainly used as protection substances against decay of the preparations comprising them. Nevertheless, it is known that undesired oxidation processes may also arise in human and animal skin. Such processes play an important role in skin aging.

Chronological skin aging is caused, for example, by endogenous, genetically determined factors. The following structural damage and functional disorders, which may also fall under the term "senile xerosis", result, for example, in the epidermis and dermis as a result of aging:

- a) dryness, roughness and formation of dryness wrinkles,
- b) itching and
- c) reduced refatting by sebaceous glands (e.g. after washing).

Exogenous factors, such as UV light and chemical noxae, can have a cumulative effect and, for example, accelerate or supplement the endogenous aging processes. In the epidermis and dermis, for example, the following structural damage and functional disorders appear in the skin in particular as a result of exogenous factors; these go beyond the extent and quality of the damage in the case of chronological aging:

- d) visible vascular dilation (teleangiectases, cuperosis);
- e) flaccidity and formation of wrinkles;
- f) local hyperpigmentation, hypopigmentation and abnormal pigmentation (e.g. age spots) and
- g) increased susceptibility to mechanical stress (e.g. cracking).

The present invention relates in particular to products for the care of skin aged naturally, and to the treatment of the damage caused by photoaging, in particular of the phenomena listed under a) to g).

Products for the care of aged skin are known per se. They comprise, for example, retinoids (vitamin A acid and/or derivatives thereof) or vitamin A and/or derivatives thereof. The degree of their effect on structural damage is, however, limited. Furthermore, in product development, there are considerable difficulties in stabilizing the active ingredients to an adequate extent against oxidative decay. The use of products comprising vitamin A acid, moreover, often causes severe erythematous skin irritations. Retinoids can therefore only be used in low concentrations.

The use of flavones and flavonoids in cosmetics and dermatology is known per se. For example, DE-44 44 238-A1 describes combinations of cinnamic acid derivatives and flavone glycosides, for example α -glycosylrutin, as antioxidants and as active ingredients against other indications. In addition, the publication JP-A Hei-04-363,395 describes a process of preventing the decomposition of perfume constituents which is characterized, inter alia, by an addition of α -glucosylrutin to the corresponding preparations. In addition, the publications EP-A 586 303 and EP-A 595 694 describe the use of flavonoids as antioxidants and/or light protection substances in cosmetics.

A considerable disadvantage of flavone derivatives, flavanone derivatives and flavonoids is, however, that they have a certain instability. A further disadvantage of these substances lies in the fact that, in relatively high concentrations, they color the products in which they are used yellow, particularly when they are used in formulations which comprise titanium dioxide. Since the consumer perceives a yellow coloration as unpleasant, this may lead in individual cases to such preparations not being marketable since they are not acceptable to or are viewed negatively by the consumer.

A further object of the present invention is therefore to remedy, or at least alleviate, the described disadvantages of the prior art.

Emulsions are generally understood as meaning heterogeneous systems which consist of two liquids which are immiscible with one another or are miscible with one another only to a limited extent, and which are usually referred to as phases. In an emulsion, one of the two liquids is dispersed in the form of very fine droplets in the other liquid.

In order to achieve permanent dispersion of one liquid in another, emulsions in the traditional sense require the addition of an interface-active substance (emulsifier). Emulsifiers have an amphiphilic molecular structure, consisting of a polar (hydrophilic) molecular moiety and a nonpolar (lipophilic) molecular moiety, which are spatially separate from one another. Emulsifiers lower the interfacial tension between the phases by positioning themselves at the interface between the two liquids. At the phase boundary, they form oil/water interfacial films, as a result of which irreversible coalescence of the droplets is prevented. Emulsions are frequently stabilized using emulsifier mixtures.

Traditional emulsifiers can, depending on their hydrophilic molecular moiety, be divided into ionic (anionic, cationic and amphoteric) and nonionic:

- The most well-known example of an anionic emulsifier is soap, the term usually used for the water-soluble sodium or potassium salts of saturated and unsaturated higher fatty acids.
- Important representatives of cationic emulsifiers are the quaternary ammonium compounds.
- The hydrophilic molecular moiety of nonionic emulsifiers often consists of glycerol, polyglycerol, sorbitans, carbohydrates and polyoxyethylene glycols and, in most cases, is linked to the lipophilic molecular moiety via ester and ether bonds. The lipophilic molecular moiety usually consists of fatty alcohols, fatty acids or isofatty acids.

By varying the structure and the size of the polar and nonpolar molecular moiety, the lipophilicity and hydrophilicity of emulsifiers can be varied within wide limits.

A decisive factor for the stability of an emulsion is the correct choice of emulsifiers. In this connection, the characteristics of all the substances present in the system are to be taken into consideration. In the case of, for example, skin care emulsions, polar oil components and, for example, UV filters lead to instabilities. In addition to the emulsifiers, therefore, other

stabilizers are also used which, for example, increase the viscosity of the emulsion and/or act as protective colloid.

Emulsions are the most important product type in the field of cosmetic and/or dermatological preparations.

The use of customary emulsifiers in cosmetic or dermatological preparations is in itself acceptable. Nevertheless, emulsifiers, like ultimately any chemical substance, may in individual instances cause allergic reactions or reactions based on oversensitivity of the user. There has therefore been no lack of attempts to reduce the amount of customary emulsifiers to a minimum, and in an ideal case even completely.

A reduction in the amount of emulsifier required can, for example, be achieved by taking advantage of the fact that very finely divided solid particles have an additional stabilizing action. This results in an accumulation of the solid substance at the oil/water phase boundary in the form of a layer, as a result of which coalescence of the disperse phases is prevented. Of fundamental importance here are not the chemical properties, but the surface properties of the solid particles.

A relatively new technical development involves stabilizing cosmetic or dermatological preparations only using very finely divided solid particles. Such "emulsifier-free" emulsions are also referred to as Pickering emulsions after their inventor.

One way of achieving solids stabilization in a cosmetic or dermatological preparation is, according to May-Alert (*Pharmazie in unserer Zeit [Pharmacy in our Time]*, Vol. 15, 1986, No. 1, 1-7), for example, to use emulsifier mixtures which comprise both anionic and also cationic surfactants. Since the mixing of anionic surfactants and cationic surfactants always results in the precipitation of insoluble, electroneutral compounds, deliberate precipitation of these neutral surfactants in the oil/water interface makes it possible to achieve additional solids stabilization in the sense of a Pickering emulsion.

In addition, WO specification WO-98/42301 describes emulsifier-free finely disperse systems of the water-in-oil type which are stabilized by the addition of micronized inorganic pigments chosen from the group of metal oxides, in particular titanium dioxide.

However, the prior art was unable to point the way to the present invention.

A further object of the present invention was to enrich the prior art with cosmetic or dermatological preparations in which any use of emulsifiers of the traditional type can be dispensed with.

Surprisingly, all of these objects are achieved by

cosmetic or dermatological preparations, which are finely disperse systems of the water-in-oil type, comprising

1. an oil phase,
2. a water phase,
3. at least one modified phyllosilicate, which exhibits both hydrophilic and lipophilic properties, i.e. which has amphiphilic character and positions itself at the water/oil interface,
4. at least one flavone, flavanone and/or flavonoid and
5. at most 0.5% by weight of one or more emulsifiers

and

optionally comprising further cosmetic or pharmaceutical auxiliaries, additives and/or active ingredients.

It is particularly advantageous according to the invention if the preparations comprise significantly less than 0.5% by weight of one or more emulsifiers. Very particular preference is given to preparations according to the invention which are entirely free from emulsifiers in the traditional sense.

The preparations according to the invention are mixtures of oils or oil-soluble substances and water or water-soluble components which are stabilized by the addition of the modified phyllosilicate particles and do not have to comprise an emulsifier in the traditional sense.

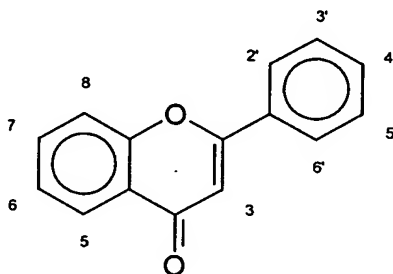
The preparations according to the invention are entirely satisfactory preparations in every respect and, surprisingly, have excellent cosmetic properties and are characterized by excellent skin compatibility. It could not have been foreseen by the person skilled in the art that the preparations according to the invention would have a better action as free-radical scavengers, would better prevent binding of harmful photoproducts to lipids, DNA and proteins, would better counter skin aging, would better protect the skin against

photoreactions and would better prevent inflammatory reactions, and would exhibit less yellowing than preparations of the prior art.

Moreover, it was surprising that in the preparations according to the invention any use of titanium dioxide and zinc oxide can be dispensed with and that in light protection preparations according to the present invention a high light protection factor and/or a high UV-A protection coupled with very good water resistance can be achieved.

Flavones, flavanones and flavonoids

Flavone and its derivatives (also often collectively called "flavones") are characterized by the following basic structure (substitution positions are shown):



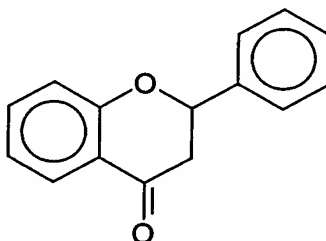
Some of the more important flavones, which are also to be found in living nature, are listed in the table below:

	OH substitution positions							
	3	5	7	8	2'	3'	4'	5'
Flavone	-	-	-	-	-	-	-	-
Flavonol	+	-	-	-	-	-	-	-
Chrysin	-	+	+	-	-	-	-	-
Galangin	+	+	+	-	-	-	-	-
Apigenin	-	+	+	-	-	-	+	-
Fisetin	+	-	+	-	-	+	+	-
Luteolin	-	+	+	-	-	+	+	-
Kaempferol	+	+	+	-	-	-	+	-
Quercetin	+	+	+	-	-	+	+	-
Morin	+	+	+	-	+	-	+	-

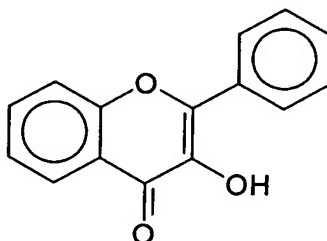
Robinetin	+	-	+	-	-	+	+	+
Gossypetin	+	+	+	+	-	+	+	-
Myricetin	+	+	+	-	-	+	+	+

In nature, flavones are usually in glycosylated form.

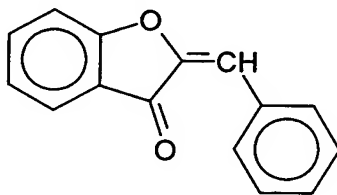
Flavonoids are glycosides of the flavones, of the flavanones, the basic framework of which is characterized by the following structure:



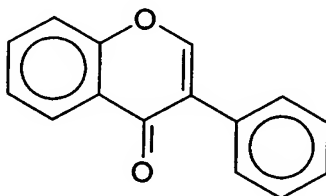
of the 3-hydroxyflavones (flavonols), the basic framework of which is characterized by the following structure:



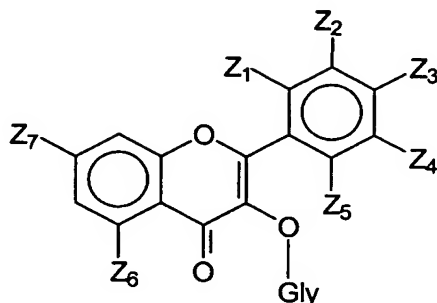
of the aurones, the basic framework of which is characterized by the following structure:



and of the isoflavones, the basic framework of which is characterized by the following structure:

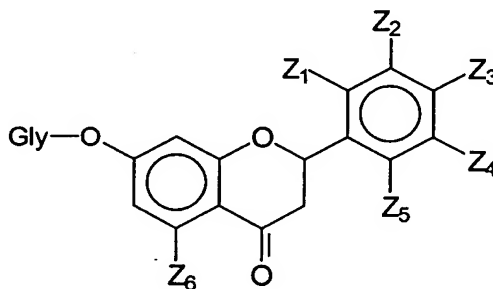


According to the invention, the flavonoids are preferably chosen from the group of substances of the generic structural formula



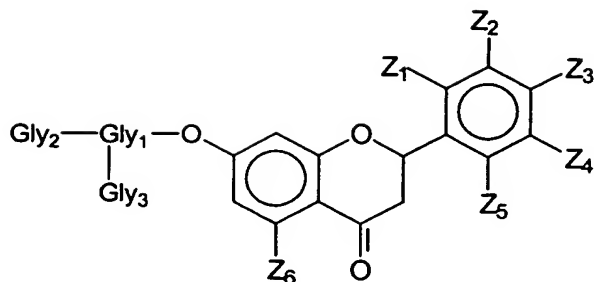
where Z₁ - Z₇, independently of one another, are chosen from the group consisting of H, OH, alkoxy and hydroxyalkoxy, where the alkoxy or hydroxyalkoxy groups may be branched or unbranched and have 1 - 18 carbon atoms, and where Gly is chosen from the group of mono- and oligoglycoside radicals.

According to the invention, the flavonoids can, however, also advantageously be chosen from the group of substances of the generic structural formula



where Z₁ - Z₆, independently of one another, are chosen from the group consisting of H, OH, alkoxy and hydroxyalkoxy, where the alkoxy or hydroxyalkoxy groups may be branched or unbranched and have 1 - 18 carbon atoms, and where Gly is chosen from the group of mono- and oligoglycoside radicals.

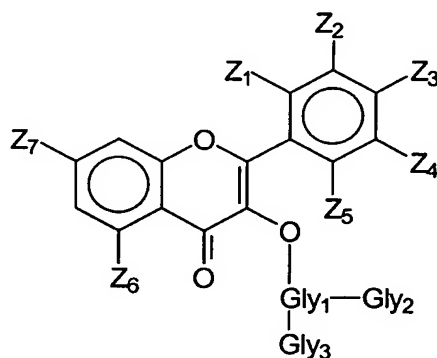
Preferably, such structures can be chosen from the group of substances of the generic structural formula



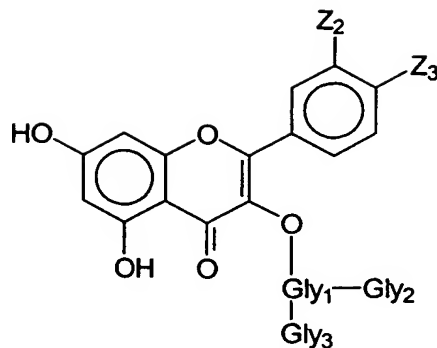
where Gly₁, Gly₂ and Gly₃, independently of one another, are monoglycoside radicals. Gly₂ and Gly₃ may also, individually or together, represent saturations by hydrogen atoms.

Preferably, Gly₁, Gly₂ and Gly₃, independently of one another, are chosen from the group of hexosyl radicals, in particular the rhamnosyl radicals and glucosyl radicals. However, other hexosyl radicals, for example allosyl, altrosyl, galactosyl, gulosyl, idosyl, mannosyl and talosyl, can also be used advantageously in some circumstances. It may also be advantageous according to the invention to use pentosyl radicals.

Z₁ - Z₅ are, independently of one another, advantageously chosen from the group consisting of H, OH, methoxy, ethoxy and 2-hydroxyethoxy, and the flavone glycosides have the structure



The flavone glycosides according to the invention are particularly advantageously chosen from the group represented by the following structure:

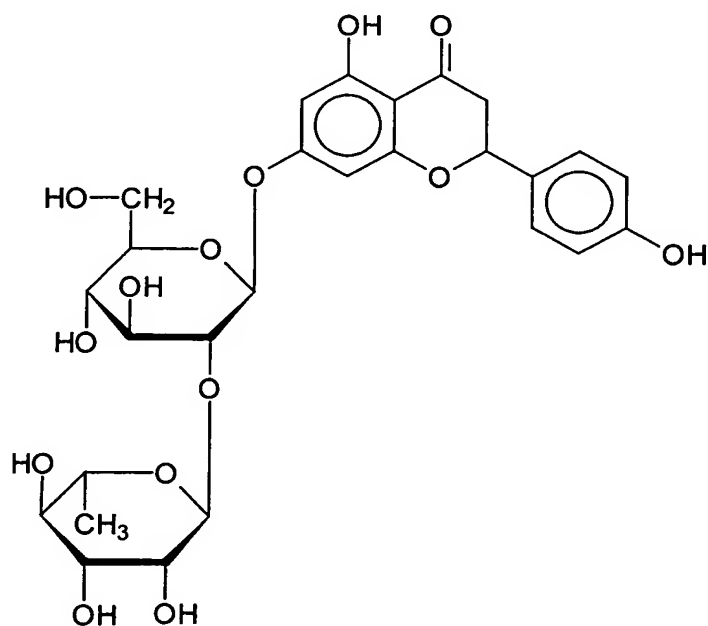
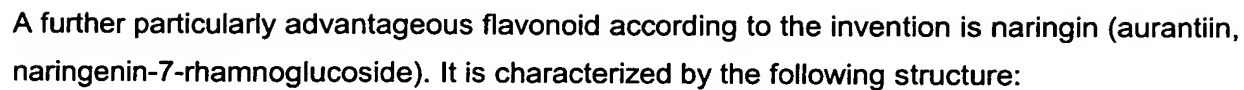


where Gly₁, Gly₂ and Gly₃, independently of one another, are monoglycoside radicals. Gly₂ and Gly₃ can also, individually or together, represent saturations by hydrogen atoms.

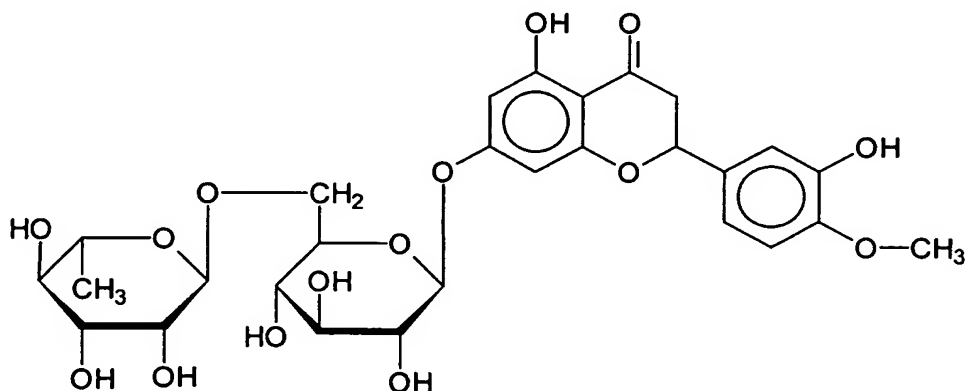
Preferably, Gly₁, Gly₂ and Gly₃, independently of one another, are chosen from the group of hexosyl radicals, in particular the rhamnosyl radicals and glucosyl radicals. However, other hexosyl radicals, for example allosyl, altrosyl, apiosyl, biosidyl, galactosyl, gulosyl, idosyl, mannosyl, talosyl, ascorbiny, arabinosyl, dulcetyl, fructosyl, mannityl, rhamnosyl, ribosyl, sorbityl, xylosyl, can also advantageously be used in some circumstances. It may also be advantageous according to the invention to use pentosyl radicals.

For the purposes of the present invention, it is particularly advantageous to choose the flavone glycoside(s) from the group consisting of α -glucosylrutin, α -glucosylmyricitrin, α -glucosylisoquercitrin and α -glucosylquercitrin.

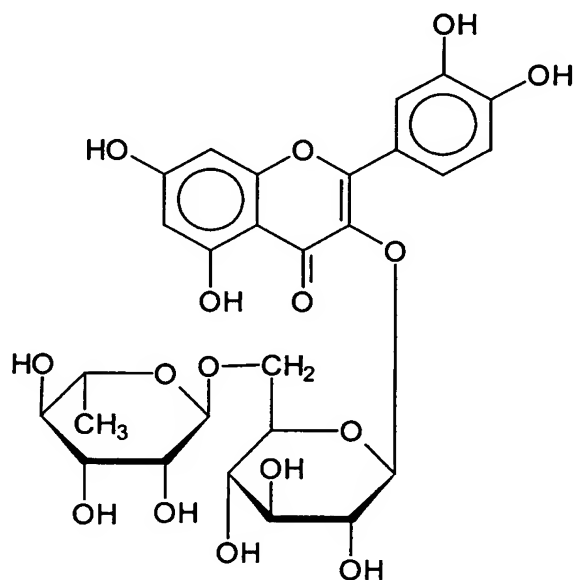
A particularly advantageous flavonoid according to the invention is α -glucosylrutin. It is characterized by the following structure:



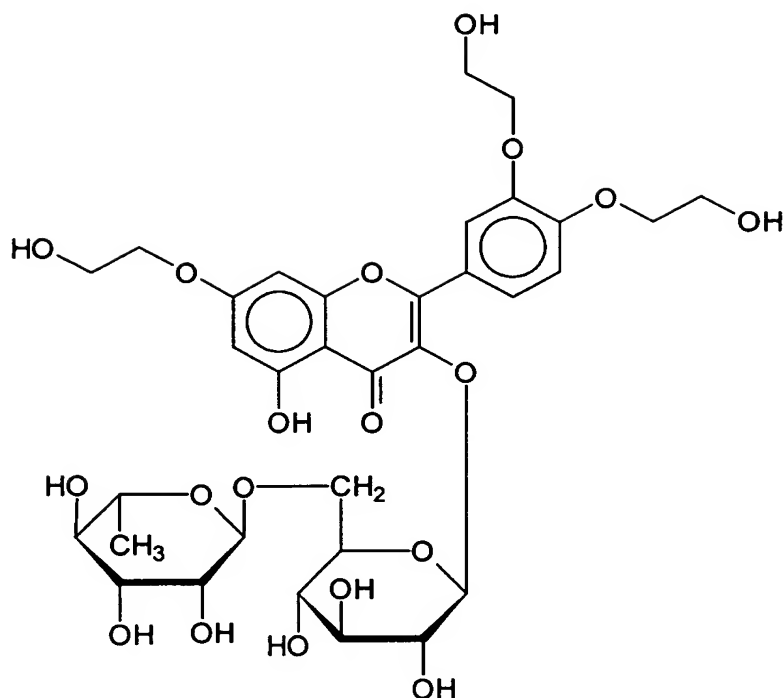
A further particularly advantageous flavonoid according to the invention is hesperidin (3',5,7-trihydroxy-4'-methoxyflavanone-7-rutinoside, hesperidoside, hesperetin-7-O-rutinoside). It is characterized by the following structure:



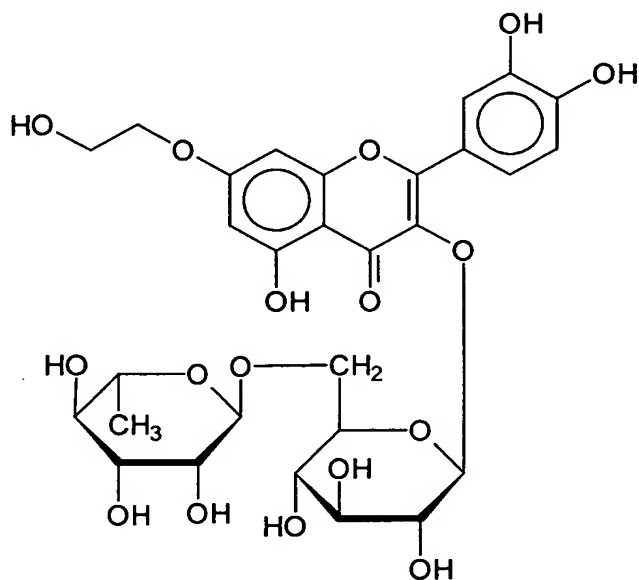
A further particularly advantageous flavonoid according to the invention is rutin (3,3',4',5,7-pentahydroxyflavone-3-rutinoside, quercetin-3-rutinoside, sophorin, birutan, rutabion, taurutin, phytomelin, melin). It is characterized by the following structure:



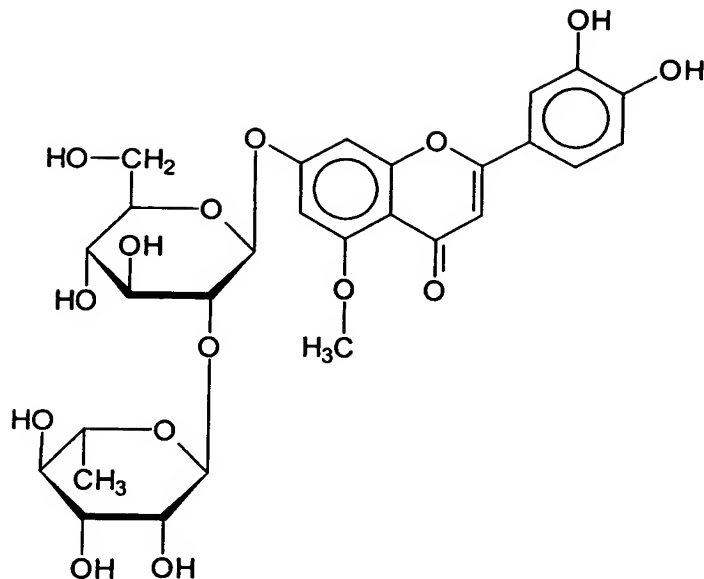
A further particularly advantageous flavonoid according to the invention is troxerutin (3,5-dihydroxy-3',4',7-tris(2-hydroxyethoxy)flavone-3-(6-O-(6-deoxy- α -L-mannopyranosyl)- β -D-glucopyranoside)). It is characterized by the following structure:



A further particularly advantageous flavonoid according to the invention is monoxerutin (3,3',4',5-tetrahydroxy-7-(2-hydroxyethoxy)flavone-3-(6-O-(6-deoxy-α-L-mannopyranosyl)-β-D-glucopyranoside)). It is characterized by the following structure:

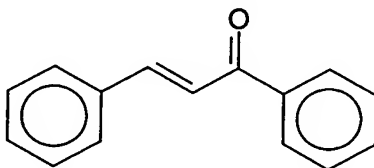


A further particularly advantageous flavonoid according to the invention is diosmin (3',5,7-trihydroxy-4'-methoxyflavone-7-rhamnoglucoside). It is characterized by the following structure:

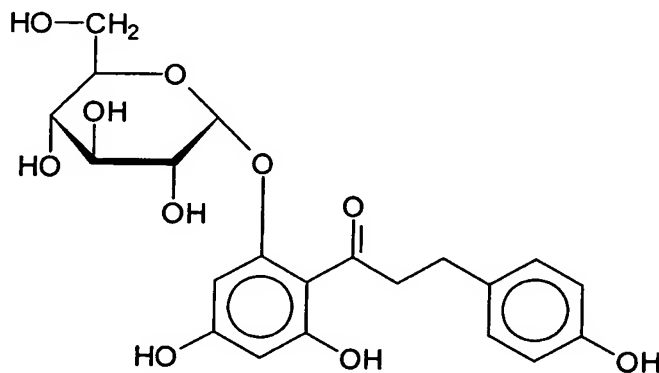


It may likewise be advantageous to use flavonoids whose glucoside radicals is or are bonded in positions 3', 4' and/or 5' via phenolic hydroxy functions of the flavone.

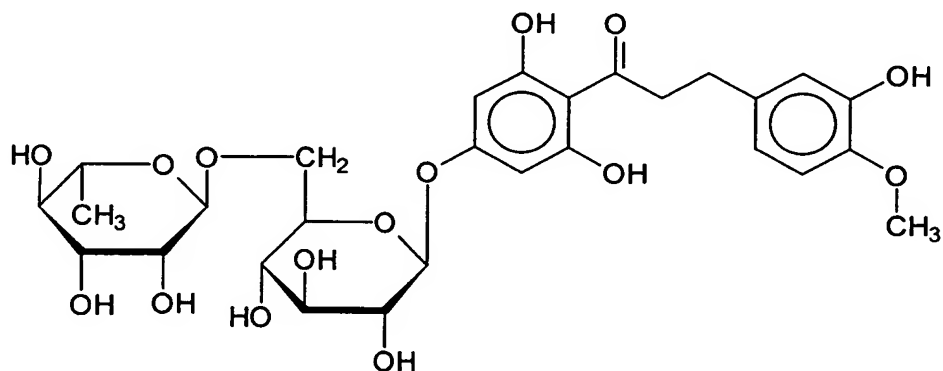
In addition, it may be advantageous to use flavonoid derivatives whose phenolic group in position 9 is free. In these cases, the term used is chalcones. The structure of the representative which gives its name to this class of substance is characterized as follows:



An advantageous representative of this class of substance is phlorizin (1-(2-(β -D-glucopyranosyloxy)-4,6-dihydroxyphenyl)-3-(4-hydroxyphenyl)-1-propanone), which is characterized by the following structure:



A further advantageous representative of this class of substance is neohesperidin dihydrochalcone (1-(4-((2-O-(6-deoxy- α -L-mannopyranosyl)- β -D-glucopyranosyl)oxy)-2,6-dihydroxyphenyl)-3-(3-hydroxy-4-methoxyphenyl)-1-propanone), which is characterized by the following structure:



The cosmetically or pharmaceutically acceptable flavone derivatives and flavanone derivatives, in particular flavonoids in the actual sense, used according to the invention are collectively referred to below as "flavonoids", irrespective of whether an individual substance or an isomer mixture or a mixture of different individual substances is present.

It may also be advantageous for the purposes of the present invention to incorporate natural, i.e. in particular vegetable, products, e.g. plant extracts, into the preparations according to the invention which are characterized by a content of cosmetically or pharmaceutically acceptable flavonoids, for example aqueous, aqueous-alcoholic or aqueous-glycolic extracts, and also dry extracts obtained in accordance with customary processes.

Those which have proven particularly advantageous are: citrus fruit peel extract, citrus fruit pip extract, soybean extract (e.g. the commercial product Phytodermin from Chem.Laboratorium Dr.Kurt Richter GmbH), Sophora japonica extract (e.g. the commercial product Sophorine from Solabia), milk thistle extract (e.g. the commercial product Psoralen Silymarin from Mani GmbH Chemische Produkte), pussytoes flower extract, spinach extract and a mixed plant extract from passion flowers, blackcurrants and vine leaves (e.g. the commercial product AE Complex from Solabia), calendula extract (e.g. the commercial product Pot Marigold AMI watersoluble from Alban Muller).

The total amount of one or more flavones, flavanones and/or flavonoids in the finished cosmetic or dermatological preparations is advantageously chosen from the range from 0.01

to 5.0% by weight, preferably 0.1 to 2.0% by weight, based on the total weight of the preparations.

Modified phyllosilicates

Silicates are salts and esters (silicic esters) of orthosilicic acid $[\text{Si}(\text{OH})_4]$ and condensation products thereof. Silicates are not only the class of minerals which contain the most types, but are also extremely important from a geological and industrial viewpoint. Over 80% of the earth's crust consists of silicates. Phyllosilicates (sheet silicates, layer silicates) are (ideally) silicate structures having two-dimensionally infinite layers of $[\text{SiO}_4]^{4-}$ tetrahedra, each tetrahedron being bonded to neighboring tetrahedra by 3 bridging oxygens.

Only approximate chemical formulae can be given for phyllosilicates since they have a large ion-exchange capability, and silicon can be replaced by aluminum, and this in turn can be replaced by magnesium, Fe^{2+} , Fe^{3+} , Zn and the like. The negative charge of the layers which may result is usually balanced by cations, in particular by Na^+ and Ca^{2+} in interlayer positions.

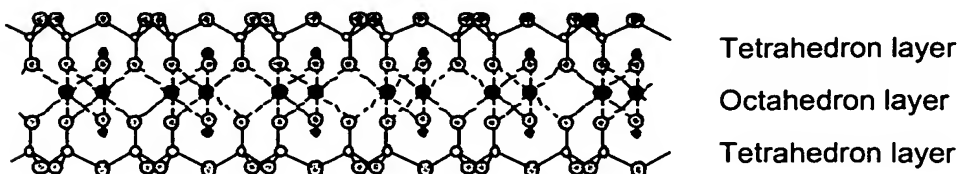
Phyllosilicates can swell by reversible intercalation of water (in a 2- to 7-fold amount) and other substances, such as, for example, alcohols, glycols and the like. Their use as thickeners in cosmetic compositions is, accordingly, known per se. However, the prior art was unable to point the way to the present invention.

Advantageous phyllosilicates for the purposes of the present invention are, for example, those whose greatest expansion direction in the unmodified and unswollen state has, on average, a length of less than 10 μm . For example, the average expansions of the modified phyllosilicate particles used can be 1000 nm x 100 nm x 1 nm and below. The effective size of the modified phyllosilicate particles in a cosmetic or dermatological formulation naturally depends on the amount of intercalated substances.

Advantageous modified phyllosilicates for the purposes of the present invention are, for example, modified smectites.

Smectites are always very finely particulate (in most cases < 2 μm) three-layer clay minerals (2:1 phyllosilicates) which occur mainly as lamella-shaped, moss-like or spherical aggregates, in which a central layer of octahedrally coordinated cations is sandwiched by two layers of $[(\text{Si},\text{Al})\text{O}_4]$ tetrahedra. Smectites are described in an idealized manner by the

following structural formula, in which circles filled in white represent silicon and/or aluminum atoms, circles filled in pale gray are oxygen atoms, circles filled in dark gray are hydrogen atoms, and circles filled in black are aluminum, magnesium, iron atoms and/or other exchange cations:



Advantageous modified smectites are, for example, modified montmorillonites. Montmorillonites are described by the approximated chemical formula $\text{Al}_2[(\text{OH})_2/\text{Si}_4\text{O}_{10}] \cdot n \text{H}_2\text{O}$ or $\text{Al}_2\text{O}_3 \cdot 4 \text{SiO}_2 \cdot \text{H}_2\text{O} \cdot n \text{H}_2\text{O}$, and are clay minerals belonging to the dioctahedral smectites.

Also particularly advantageous for the purposes of the present invention are, for example, modified hectorites. Hectorites are types of smectites and have the approximated chemical formula $\text{M}^+_{0.3}(\text{Mg}_{2.7}\text{Li}_{0.3})[\text{Si}_4\text{O}_{10}(\text{OH})_2]$, in which M^+ is in most cases Na^+ .

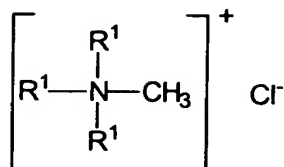
Also advantageous for the purposes of the present invention are modified bentonites. Bentonites are clays and rocks which contain smectites, especially montmorillonite, as main minerals. The "crude" bentonites are either calcium bentonites (referred to in Great Britain as fuller's earths) or sodium bentonites (also: Wyoming bentonites).

Modified phyllosilicates for the purposes of the present invention are phyllosilicates, in particular the phyllosilicate types already mentioned, whose organophilicity (also: lipophilicity) has been increased, for example by reaction with quaternary ammonium compounds. Such phyllosilicates are also referred to as organophilic phyllosilicates.

Particularly advantageous for the purposes of the present invention are bentones, i.e. organic derivatives of montmorillonites (or bentonites) and/or hectorites, which are prepared by ion-exchange reactions with alkylammonium bases.

Advantageous modified phyllosilicates for the purposes of the present invention are obtainable, for example, by reacting phyllosilicates with quaternium-18. Quaternium-18 is a

mixture of quaternary ammonium chloride salts which are described by the following structural formula:



in which

the radicals R^1 are independently of one another chosen from the group consisting of methyl and hydrogenated tallow radicals having a chain length of from 12 to 20 carbon atoms.

According to the invention, particular preference is given to stearalkonium hectorite, a reaction product of hectorite and stearalkonium chloride (benzyltrimethylstearylammmonium chloride), and quaternium-18 hectorite, a reaction product of hectorite and quaternium-18, which are available, for example, under the trade names Bentone 27 and Bentone 38 from Nordmann & Rassmann.

The total amount of one or more modified phyllosilicates in the finished cosmetic or dermatological preparations is advantageously chosen from the range 0.05 to 20.0% by weight, preferably 0.1 to 5.0% by weight, based on the total weight of the preparations.

Although it is particularly preferred to stabilize the preparations according to the invention only by the addition of one or more modified phyllosilicates, it may also be advantageous to combine the modified phyllosilicate particles with further amphiphilic pigments which may also contribute to the stabilization of the Pickering emulsions.

Such pigments are, for example, micronized, inorganic pigments chosen from the group of amphiphilic metal oxides, in particular from the group consisting of titanium dioxide, zinc oxide, silicon dioxide and silicates (e.g. talc), it being possible for the metal oxides to be present individually or as a mixture. In this connection, it is essentially unimportant in which of the potentially naturally occurring modifications the amphiphilic metal oxides used are present.

It is advantageous to choose the average particle diameter of the pigments used for the combination with modified phyllosilicates to be between 1 nm and 200 nm, particularly advantageously between 5 nm and 100 nm.

For the purposes of the present invention, it is advantageous to combine the modified phyllosilicates according to the invention with untreated, virtually pure pigment particles, in particular with those which can also be used as dye in the food industry and/or as absorbers of UV radiation in sunscreens. Advantageous examples are the zinc oxide pigments available from Merck, and those available under the trade names Zinkoxid neutral from Haarmann & Reimer or NanoX from Harcros Chemical Group.

Also advantageous according to the invention is the combination of modified phyllosilicates with inorganic pigments which have been surface-treated ("coated") to repel water, the intention being for the amphiphilic character of these pigments to be formed or retained at the same time. This surface treatment may involve providing the pigments with a thin hydrophobic layer by methods known per se.

Such a process, which is described below using titanium dioxide as an example, consists, for example, in producing the hydrophobic surface layer by a reaction in accordance with



n and m are stoichiometric parameters to be used as desired, and R and R' are the desired organic radicals. Particularly advantageous combination partners are TiO_2 pigments, for example those coated with aluminum stearate and obtainable under the trade name MT 100 T from TAYCA.

A further advantageous coating of the combination partners consists of dimethylpolysiloxane (also: dimethicone), a mixture of completely methylated, linear siloxane polymers which have been terminally blocked with trimethylsiloxy units. Particularly advantageous for the purposes of the present invention is the combination of modified phyllosilicates with zinc oxide pigments which have been coated in this manner.

It is also advantageous if the inorganic pigments used in addition to modified phyllosilicates have been coated with a mixture of dimethylpolysiloxane, in particular dimethylpolysiloxane having an average chain length of from 200 to 350 dimethylsiloxane units, and silica gel, which is also referred to as simethicone. It is particularly advantageous if the inorganic pigments have been additionally coated with aluminum hydroxide or hydrated aluminum oxide (also: alumina, CAS No.: 1333-84-2). Particularly advantageous combination partners

are titanium dioxides which have been coated with simethicone and alumina, it also being possible for the coating to comprise water. One example thereof is the titanium dioxide available under the trade name Eusolex T2000 from Merck.

Also advantageous for the purposes of the present invention is the combination of modified phyllosilicates with a mixture of different inorganic, amphiphilic pigment types, either within a crystal, for example as iron mixed oxide or talc (magnesium silicate) or else by mixing two or more types of metal oxide within a preparation. Particularly advantageous combination partners are magnesium silicates, for example those available under the trade name Talkum Micron from Grolmann.

The modified phyllosilicates according to the invention can also advantageously be combined with further pigments, for example, with titanium dioxide pigments which have been coated with octylsilanol, and/or with silicon dioxide particles which have been surface-treated to repel water. Suitable silicon dioxide particles for the combination are, for example, spherical polyalkylsilsesquioxane particles, as mentioned in European Laid-Open Specification 0 686 391. Such polyalkylsilsesquioxane particles are available, for example, under the trade names Aerosil R972 and Aerosil 200V from Degussa.

It is further advantageous to combine the modified phyllosilicates with microfine polymer particles which are in the preparation in the form of solids. Favorable examples of combination partners for the purposes of the present invention are polycarbonates, polyethers, polyethylene, polypropylene, polyvinyl chloride, polystyrene, polyamides, polyacrylates and the like.

Examples of combination partners suitable according to the invention are microfine polyamide particles, in particular those available under the trade name SP-500 from TORAY. Also advantageous are polyamide 6 (also: nylon 6) and polyamide 12 (also: nylon 12) particles. Polyamide 6 is the polyamide [poly(ϵ -caprolactam)], built up from ϵ -aminocaproic acid (6-aminohexanoic acid) or ϵ -caprolactam, and polyamide 12 is a poly(ϵ -laurolactam) of ϵ -laurolactam. Advantageous examples for the purposes of the present invention are Orgasol[®] 1002 (polyamide 6) and Orgasol[®] 2002 (polyamide 12) from ELF ATOCHEM.

Further advantageous microfine polymer particles which are suitable for combination with the modified phyllosilicates according to the invention are microfine polymethacrylates. Such

particles are available, for example, under the trade name POLYTRAP from DOW CHEMICAL.

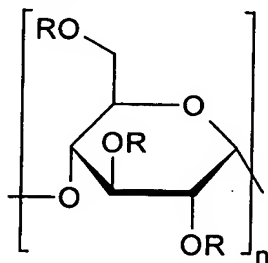
It is particularly advantageous, although not obligatory, if the microfine polymer particles used as combination partners have been surface-coated. This surface treatment can involve providing the polymer particles with a thin hydrophilic layer by processes known per se. Advantageous coatings consist, for example, of titanium dioxide (TiO_2), zirconium dioxide (ZrO_2) or else further polymers, such as, for example, polymethyl methacrylate. Particularly advantageous microfine polymer particles for the purposes of the present invention are, for example, those available by the process described in US Patent Specification 4,898,913 for the hydrophilic coating of hydrophobic polymer particles.

The average particle diameter of the microfine polymer particles used as combination partners is preferably chosen to be less than $100\text{ }\mu\text{m}$, particularly advantageously to be less than $50\text{ }\mu\text{m}$. In this connection, it is essentially unimportant in which form (platelets, rods, spherules etc.) the polymer particles used are present.

The modified phyllosilicates according to the invention are also preferably combined with amphiphilic modified polysaccharides which do not exhibit thickening properties.

Such amphiphilic polysaccharides are obtainable, for example, by reacting starch with mono-, bi- or polyfunctional reagents or oxidizing agents in reactions which proceed in a predominantly polymer-analogous manner.

These reactions are based essentially on modifications of the hydroxyl groups of the polyglucans by etherification, esterification or selective oxidation. This produces, for example, starch ethers and starch esters of general structural formula

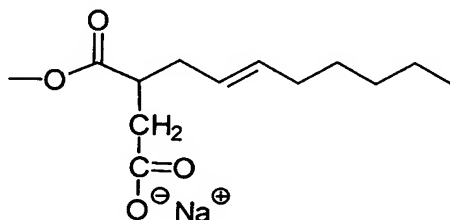


structural formula (I)

in which R can, for example, be a hydrogen and/or an alkyl and/or aralkyl radical (in the case of starch ethers) or a hydrogen and/or an organic and/or an inorganic acid radical (in the case of starch esters). Starch ethers and starch esters are advantageous combination partners for the purposes of the present invention.

It is particularly advantageous to combine the modified phyllosilicates according to the invention with starch ethers, e.g. with those obtainable by etherifying starch with tetramethylolacetylenediurea and which are referred to as Amylum non mucilaginosum (nonswelling starch).

Also particularly advantageous is the combination of modified phyllosilicates according to the invention with starch esters and/or salts thereof, for example with sodium and/or aluminum salts of half-esters of starch which have low degrees of substitution, in particular with sodium starch n-octenyl succinate of the structural formula (I) in which R is characterized by the following structure



and which is available, for example, under the trade name Amiogum® 23 from CERESTAR, and with aluminum starch octenyl succinate, in particular with those available under the trade names Dry Flo® Elite LL and Dry Flo® PC from CERESTAR.

It is advantageous to choose the average particle diameter of the modified polysaccharides used for the combination with the modified phyllosilicates according to the invention to be less than 20 µm, particularly advantageously less than 15 µm.

The list of given modified polysaccharides which can be combined with the modified phyllosilicates is not of course intended to be limiting. Modified polysaccharides which are advantageous combination partners for the purposes of the present invention are obtainable in numerous ways, either chemical or physical in nature, which are known per se. For the preparation of such polysaccharides, novel ways are in principle also conceivable. In this connection, it is important that the modified polysaccharides display amphiphilic properties and that they do not have a thickening action.

The modified phyllosilicates according to the invention are also preferably combined with boron nitride.

Advantageous combination partners for the purposes of the present invention are, for example, the boron nitrides listed below:

Trade name	Obtainable from:
Boron Nitride Powder	Advanced Ceramics
Boron Nitride Powder	Sintec Keramik
Ceram Blanche	Kawasaki
HCST Boron Nitride	Stark
Très BN [®]	Carborundum
Wacker-Bornitrid BNP	Wacker-Chemie

It is advantageous to choose the average particle diameter of the boron nitride particles used to be less than 20 µm, particularly advantageously less than 15 µm.

Likewise advantageous combination partners are boron nitride particles which have been surface-treated ("coated") to repel water, the intention being for the amphiphilic character to be simultaneously formed or retained.

An advantageous coating of the boron nitride particles consists of dimethylpolysiloxane (also: dimethicone), a mixture of completely methylated, linear siloxane polymers which have been terminally blocked with trimethylsiloxy units. The boron nitride particles treated with dimethicone and obtainable from Carborundum under the trade name Très BN[®] UHP 1106, for example, are advantageous.

Also advantageous is a coating of the boron nitride particles with polymethylhydrogen-siloxane, a linear polysiloxane, which is also referred to as methicone. Advantageous boron particles coated with methicone are, for example, those obtainable from Carborundum under the trade name Très BN[®] UHP 1107.

In all of the abovementioned cases, it is advantageous to choose the overall concentration of all pigments to be greater than 0.05% by weight, particularly advantageously between 0.05% by weight and 30% by weight, based on the total weight of the preparations, where the

concentration of modified phyllosilicates – likewise based on the total weight of the preparations – for the purposes of the present invention is preferably to be chosen from the range 0.05% by weight to 20% by weight, advantageously 0.1% by weight to 5% by weight.

The Pickering emulsions according to the invention can be used as bases for cosmetic or dermatological formulations. The latter can have the customary composition and be used, for example, for the treatment and care of the skin, as lip care product, as deodorant product and as make-up or make-up remover product in decorative cosmetics or as a light protection preparation. For use, the cosmetic and dermatological preparations according to the invention are applied to the skin in a sufficient amount in the manner customary for cosmetics.

Accordingly, for the purposes of the present invention, cosmetic or topical dermatological compositions can, depending on their composition, be used, for example, as skin protection cream, cleansing milk, sunscreen lotion, nourishing cream, day or night cream etc. In some instances, it is possible and advantageous to use the compositions according to the invention as bases for pharmaceutical formulations.

The cosmetic and dermatological preparations according to the invention can comprise cosmetic auxiliaries, as are customarily used in such preparations, e.g. preservatives, bactericides, perfumes, antifoams, dyes, pigments which have a coloring action, thickeners, emollients, moisturizers and/or humectants, fats, oils, waxes or other customary constituents of a cosmetic or dermatological formulation, such as alcohols, polyols, polymers, foam stabilizers, electrolytes, organic solvents or silicone derivatives.

A surprising property of the preparations according to the invention is that they are very good vehicles for cosmetic or dermatological active ingredients into the skin, advantageous active ingredients being antioxidants which are able to protect the skin against oxidative stress.

According to the invention, the preparations advantageously comprise one or more antioxidants. Antioxidants which are favorable, but nevertheless optional, are all antioxidants which are suitable or customary for cosmetic and/or dermatological applications. It is advantageous to use antioxidants as the sole active ingredient class when, for example, a cosmetic or dermatological application is at the fore, such as, for example, the control of oxidative stress of the skin. It is, however, also favorable to provide the stick preparations

according to the invention with a content of one or more antioxidants if the intention is for the preparations to have another purpose, e.g. as sunscreens.

The antioxidants are particularly advantageously chosen from the group consisting of amino acids (e.g. glycine, histidine, tyrosine, tryptophan) and derivatives thereof, imidazoles, (e.g. urocanic acid) and derivatives thereof, peptides, such as D,L-carnosine, D-carnosine, L-carnosine and derivatives thereof (e.g. anserine), carotenoids, carotenes (e.g. α -carotene, β -carotene, lycopene) and derivatives thereof, chlorogenic acid and derivatives thereof, lipoic acid and derivatives thereof (e.g. dihydrolipoic acid), aurothioglucose, propylthiouracil and other thiols (e.g. thioredoxin, glutathione, cysteine, cystine, cystamine and the glycosyl, N-acetyl, methyl, ethyl, propyl, amyl, butyl and lauryl, palmitoyl, oleyl, γ -linoleyl, cholesteryl and glyceryl esters thereof) and salts thereof, dilauryl thiodipropionate, distearyl thiodipropionate, thiodipropionic acid and derivatives thereof (esters, ethers, peptides, lipids, nucleotides, nucleosides and salts) and sulfoximine compounds (e.g. buthionine sulfoximines, homocysteine sulfoximine, buthionine sulfones, penta-, hexa-, heptathionine sulfoximines) in very low tolerated doses (e.g. pmol to μ mol/kg), and also (metal) chelating agents (e.g. α -hydroxyfatty acids, palmitic acid, phytic acid, lactoferrin), α -hydroxy acids (e.g. citric acid, lactic acid, malic acid), humic acid, bile acid, bile extracts, bilirubin, biliverdin, EDTA, EGTA and derivatives thereof, unsaturated fatty acids and derivatives thereof (e.g. γ -linolenic acid, linoleic acid, oleic acid), folic acid and derivatives thereof, ubiquinone and ubiquinol and derivatives thereof, vitamin C and derivatives (e.g. ascorbyl palmitate, Mg ascorbyl phosphate, ascorbyl acetate), tocopherols and derivatives (e.g. vitamin E acetate), vitamin A and derivatives (vitamin A palmitate) and coniferyl benzoate of benzoin resin, rutinic acid and derivatives thereof, α -glycosylrutin, ferulic acid, furfurylidene-glucitol, carnosine, butylhydroxytoluene, butylhydroxyanisole, nordihydroguaiacic acid, nordihydroguaiaretic acid, trihydroxybutyrophenone, uric acid and derivatives thereof, mannose and derivatives thereof, zinc and derivatives thereof (e.g. ZnO, ZnSO₄), selenium and derivatives thereof (e.g. selenomethionine), stilbenes and derivatives thereof (e.g. stilbene oxide, trans-stilbene oxide), and the derivatives (salts, esters, ethers, sugars, nucleotides, nucleosides, peptides and lipids) of said active substances which are suitable according to the invention.

The amount of abovementioned antioxidants (one or more compounds) in the preparations according to the invention is preferably 0.001 to 30% by weight, particularly preferably 0.05 to 20% by weight, in particular 0.1 to 10% by weight, based on the total weight of the preparation.

If vitamin E and/or derivatives thereof are the antioxidant(s), it is advantageous to choose their respective concentrations from the range 0.001 to 10% by weight, based on the total weight of the formulation.

If vitamin A or vitamin A derivatives, or carotenes or derivatives thereof are the antioxidant(s), it is advantageous to choose their respective concentrations from the range 0.001 to 10% by weight, based on the total weight of the formulation.

According to the invention, the active ingredients (one or more compounds) can also very advantageously be chosen from the group of lipophilic active ingredients, in particular from the following group:

Acetylsalicylic acid, atropine, azulene, hydrocortisone and derivatives thereof, e.g. hydrocortisone-17 valerate, vitamins, e.g. ascorbic acid and derivatives thereof, vitamins of the B and D series, very favorably vitamin B₁, vitamin B₁₂ and vitamin D₁, but also bisabolol, unsaturated fatty acids, namely the essential fatty acids (often also called vitamin F), in particular gamma-linolenic acid, oleic acid, eicosapentaenoic acid, docosahexaenoic acid and derivatives thereof, chloramphenicol, caffeine, prostaglandins, thymol, camphor, extracts or other products of a vegetable or animal origin, e.g. evening primrose oil, starflower oil or currant seed oil, fish oils, cod-liver oil or also ceramides and ceramide-like compounds and so on.

It is also advantageous to choose the active ingredients from the group of refatting substances, for example purcellin oil, Eucerit® and Neocerit®.

The list of specified active ingredients or active ingredient combinations which can be used in the Pickering emulsions according to the invention should not of course be limiting.

Cosmetic and dermatological preparations which are in the form of a sunscreen are also favorable. In addition to the active ingredient combinations according to the invention, these preferably additionally comprise at least one UV-A filter substance and/or at least one UV-B filter substance. Such formulations can, although it is not necessary, optionally also comprise one or more inorganic pigments as UV filter substances.

Inorganic pigments based on metal oxides and/or other metal compounds which are insoluble or virtually insoluble in water are preferably present, in particular the oxides of titanium (TiO_2), zinc (ZnO), iron (e.g. Fe_2O_3), zirconium (ZrO_2), silicon (SiO_2), manganese (e.g. MnO), aluminum (Al_2O_3), cerium (e.g. Ce_2O_3), mixed oxides of the corresponding metals, and mixtures of such oxides.

An additional content of stabilizing titanium dioxide and/or zinc oxide particles can of course also be advantageous, but is not necessary for the purposes of the present invention.

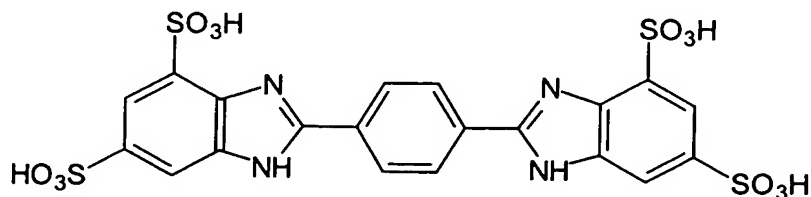
For the purposes of the present invention, it is also advantageous to prepare cosmetic and dermatological preparations whose main purpose is not protection against sunlight, but which nevertheless contain UV protection substances. Thus, for example, UV-A and UV-B filter substances are usually incorporated into day creams.

Also, UV protectants, like antioxidants, and if desired, preservatives, provide effective protection of the preparations themselves against spoilage.

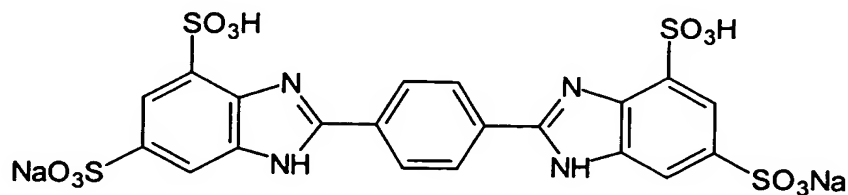
Preparations according to the invention advantageously comprise substances which absorb UV radiation in the UV-A and/or UV-B region, the total amount of filter substances being, for example, from 0.1% by weight to 30% by weight, preferably from 0.5 to 20% by weight, in particular from 1.0 to 15% by weight, based on the total weight of the preparations, in order to provide cosmetic preparations which protect the hair and the skin from the entire range of ultraviolet radiation. They can also be used as sunscreens for the hair or the skin.

Advantageous UV-A filter substances for the purposes of the present invention are dibenzoylmethane derivatives, in particular 4-(tert-butyl)-4'-methoxydibenzoylmethane (CAS No. 70356-09-1), which is sold by Givaudan under the name Parsol® 1789 and by Merck under the trade name Eusolex® 9020.

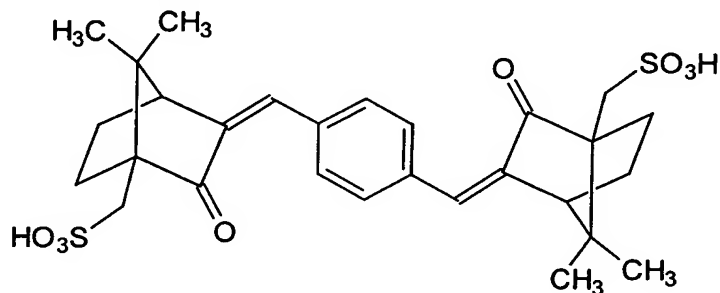
Further advantageous UV-A filter substances are phenylene-1,4-bis-(2-benzimidazolyl)-3,3'-5,5'-tetrasulfonic acid:



and its salts, particularly the corresponding sodium, potassium or triethanolammonium salts, in particular phenylene-1,4-bis-(2-benzimidazolyl)-3,3'-5,5'-tetrasulfonic bis-sodium salt:

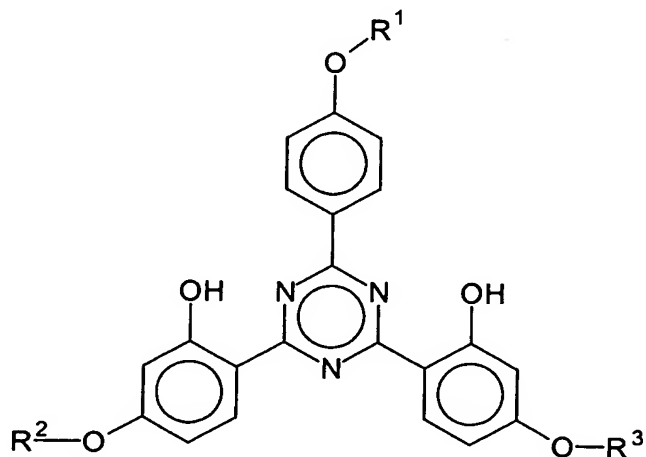


and 1,4-di(2-oxo-10-sulfo-3-bornylidenemethyl)benzene and salts thereof (in particular the corresponding 10-sulfato compounds, in particular the corresponding sodium, potassium or triethanolammonium salt), which is also referred to as benzene-1,4-di(2-oxo-3-bornylidenemethyl-10-sulfonic acid) and is characterized by the following structure:



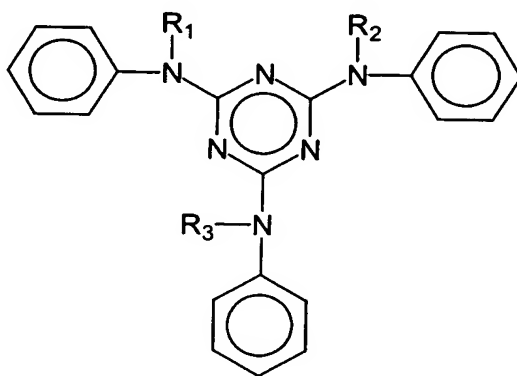
Advantageous UV filter substances for the purposes of the present invention are also broadband filters, i.e. filter substances which absorb both UV-A and also UV-B radiation.

Advantageous broadband filters or UV-B filter substances are, for example, bisresorcinyltriazine derivatives having the following structure:

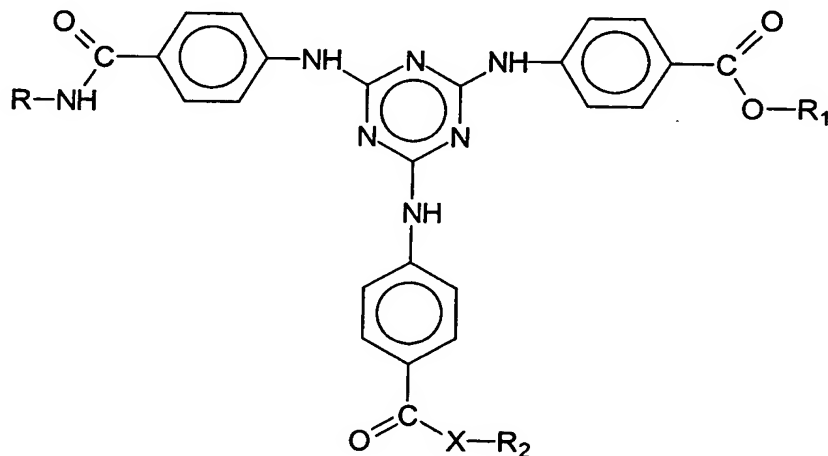


where R^1 , R^2 and R^3 independently of one another are chosen from the group of branched and unbranched alkyl groups having 1 to 10 carbon atoms, or are a single hydrogen atom. Particular preference is given to 2,4-bis[[4-(2-ethylhexyloxy)-2-hydroxy]phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine (INCI: Aniso Triazine), which is available under the trade name Tinosorb® S from CIBA-Chemikalien GmbH and to tris(2-ethylhexyl) 4,4',4''-(1,3,5-triazine-2,4,6-triyltriimino)trisbenzoate, synonym: 2,4,6-tris[anilino-(p-carbo-2'-ethyl-1'-hexyloxy)]-1,3,5-triazine (INCI: Octyl Triazone), which is marketed by BASF Aktiengesellschaft under the trade name UVINUL® T 150.

Other UV filter substances, which have the structural formula



are also advantageous UV filter substances for the purposes of the present invention, for example the s-triazine derivatives described in European Laid-Open Specification EP 570 838 A1, whose chemical structure is expressed by the generic formula

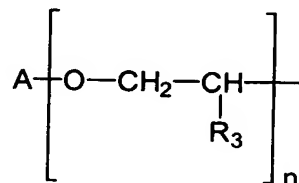


where

R is a branched or unbranched C_1 - C_{18} -alkyl radical, a C_5 - C_{12} -cycloalkyl radical, optionally substituted with one or more C_1 - C_4 -alkyl groups,

X is an oxygen atom or an NH group,

R_1 is a branched or unbranched C_1 - C_{18} -alkyl radical, a C_5 - C_{12} -cycloalkyl radical, optionally substituted by one or more C_1 - C_4 -alkyl groups, or a hydrogen atom, an alkali metal atom, an ammonium group or a group of the formula



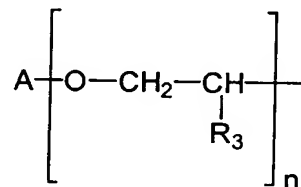
in which

A is a branched or unbranched C_1 - C_{18} -alkyl radical, a C_5 - C_{12} -cycloalkyl or aryl radical, optionally substituted by one or more C_1 - C_4 -alkyl groups,

R_3 is a hydrogen atom or a methyl group,

n is a number from 1 to 10,

R_2 is a branched or unbranched C_1 - C_{18} -alkyl radical, a C_5 - C_{12} -cycloalkyl radical, optionally substituted by one or more C_1 - C_4 -alkyl groups, when X is the NH group, and a branched or unbranched C_1 - C_{18} -alkyl radical, a C_5 - C_{12} -cycloalkyl radical, optionally substituted by one or more C_1 - C_4 -alkyl groups, or a hydrogen atom, an alkali metal atom, an ammonium group or a group of the formula



in which

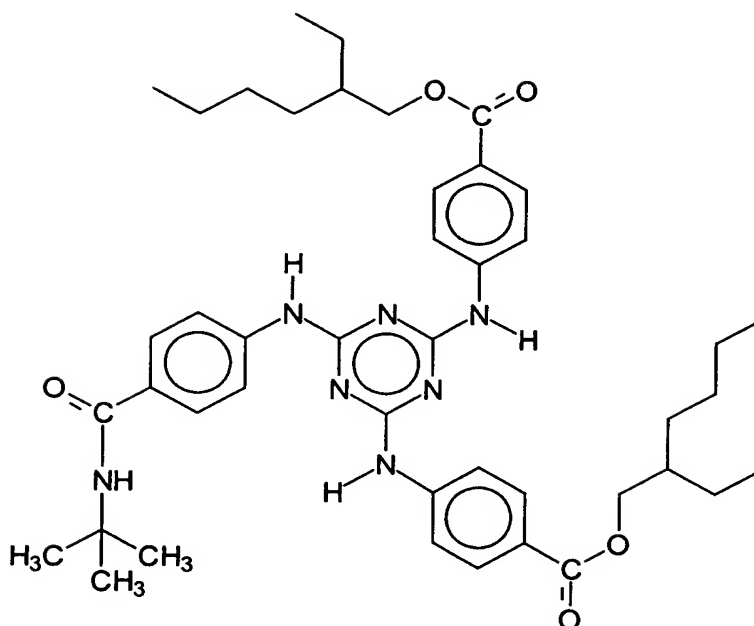
A is a branched or unbranched C_1 - C_{18} -alkyl radical, a C_5 - C_{12} -cycloalkyl or aryl radical, optionally substituted by one or more C_1 - C_4 -alkyl groups,

R_3 is a hydrogen atom or a methyl group,

n is a number from 1 to 10,

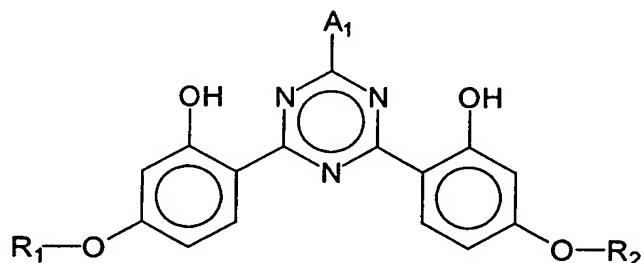
when X is an oxygen atom.

A particularly preferred UV filter substance for the purposes of the present invention is also an unsymmetrically substituted s-triazine, the chemical structure of which is expressed by the formula



and which is also referred to below as diethylbutylamidotriazone (INCI: diethylbutamidotriazone) and is available under the trade name UVASORB HEB from Sigma 3V.

European Laid-Open Specification 775 698 also describes preferred bisresorcinyltriazine derivatives, the chemical structure of which is expressed by the generic formula

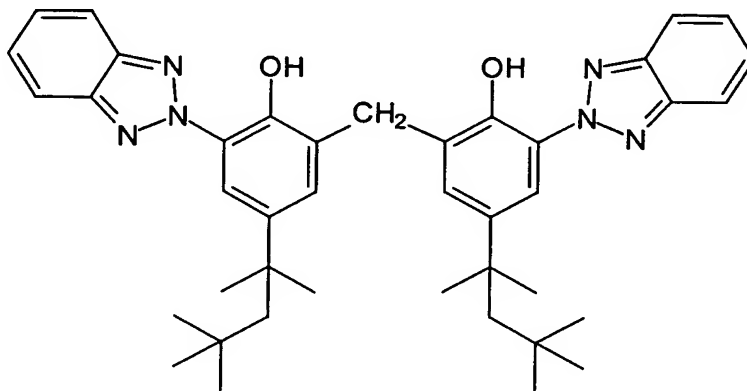


where R_1 , R_2 and A_1 represent very different organic radicals.

Also advantageous for the purposes of the present invention are 2,4-bis{[4-(3-sulfonato)-2-hydroxypropyloxy]-2-hydroxy}phenyl-6-(4-methoxyphenyl)-1,3,5-triazine sodium salt, 2,4-bis{[4-(3-(2-propyloxy)-2-hydroxypropyloxy)-2-hydroxy]phenyl}-6-(4-methoxyphenyl)-1,3,5-triazine, 2,4-bis{[4-(2-ethylhexyloxy)-2-hydroxy]phenyl}-6-[4-(2-methoxyethylcarboxyl)-phenylamino]-1,3,5-triazine, 2,4-bis{[4-(3-(2-propyloxy)-2-hydroxypropyloxy)-2-hydroxy]phenyl}-6-[4-(2-ethylcarboxyl)phenylamino]-1,3,5-triazine, 2,4-bis{[4-(2-ethylhexyloxy)-2-hydroxy]phenyl}-6-(1-methylpyrrol-2-yl)-1,3,5-triazine, 2,4-bis{[4-tris(trimethylsiloxy)silylpropyloxy]-2-hydroxy}phenyl}-6-(4-methoxyphenyl)-1,3,5-triazine, 2,4-

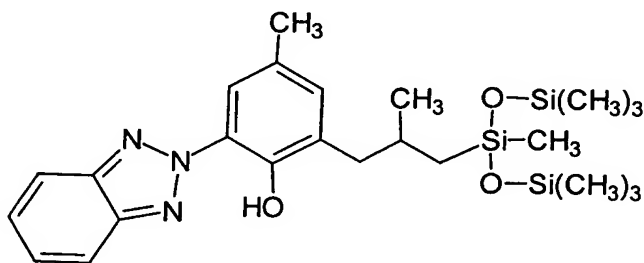
bis[[4-(2"-methylpropenyloxy)-2-hydroxy]phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine and 2,4-bis[[4-(1',1',1',3',5',5',5'-heptamethylsiloxy-2"-methylpropyloxy)-2-hydroxy]phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine.

An advantageous broadband filter for the purposes of the present invention is 2,2'-methylenebis(6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol), which is characterized by the chemical structural formula



and is available under the trade name Tinosorb® M from CIBA-Chemikalien GmbH.

Another advantageous broadband filter for the purposes of the present invention is 2-(2H-benzotriazol-2-yl)-4-methyl-6-[2-methyl-3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propyl]phenol (CAS No.: 155633-54-8) having the INCI name Drometrizole Trisiloxane, which is characterized by the chemical structural formula



The UV-B filters can be oil-soluble or water-soluble. Examples of advantageous oil-soluble UV-B filter substances are:

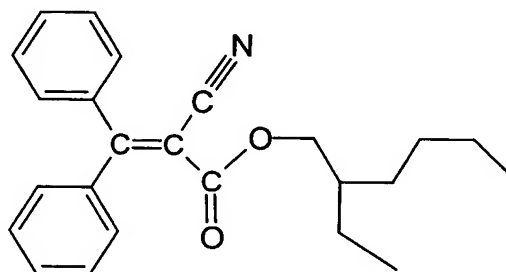
- 3-benzylidenecamphor derivatives, preferably 3-(4-methylbenzylidene)camphor, 3-benzylidenecamphor;
- 4-aminobenzoic acid derivatives, preferably 2-ethylhexyl 4-(dimethylamino)benzoate, amyl 4-(dimethylamino)benzoate;
- 2,4,6-trianilino(p-carbo-2'-ethyl-1'-hexyloxy)-1,3,5-triazine;

- esters of benzalmalonic acid, preferably di(2-ethylhexyl) 4-methoxybenzalmalonate,
- esters of cinnamic acid, preferably 2-ethylhexyl 4-methoxycinnamate, isopentyl 4-methoxycinnamate;
- derivatives of benzophenone, preferably 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxy-4'-methylbenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone
- and UV filters bonded to polymers.

Examples of advantageous water-soluble UV-B filter substances are:

- salts of 2-phenylbenzimidazole-5-sulfonic acid, such as its sodium, potassium or its triethanolammonium salt, and also the sulfonic acid itself;
- sulfonic acid derivatives of 3-benzylidenecamphor, such as, for example, 4-(2-oxo-3-bornylidenemethyl)benzenesulfonic acid, 2-methyl-5-(2-oxo-3-bornylidenemethyl)-sulfonic acid and salts thereof.

A further light protection filter substance which can be used advantageously according to the invention is ethylhexyl 2-cyano-3,3-diphenylacrylate (octocrylene), which is available from BASF under the name Uvinul® N 539 and is characterized by the following structure:



It can also be of considerable advantage to use polymer-bonded or polymeric UV filter substances in preparations according to the present invention, in particular those described in WO-A-92/20690.

In some instances, it may also be advantageous to incorporate further UV-A and/or UV-B filters in accordance with the invention into cosmetic or dermatological preparations, for example certain salicylic acid derivatives, such as 4-isopropylbenzyl salicylate, 2-ethylhexyl salicylate (= octyl salicylate), homomenthyl salicylate.

The list of given UV filters which can be used for the purposes of the present invention is not of course intended to be limiting.

The examples below serve to illustrate the present invention without limiting it. The numerical values in the examples are percentages by weight, based on the total weight of the respective preparations.

[illegible]